Volume Measurements of Laser-generated Pits for In Situ Geochronology Using KArLE (Potassium-Argon Laser Experiment)

R.A French[1], B.A. Cohen[2], and J.S. Miller[3]

[1]Dept. of Earth and Planetary Sciences, Northwestern University, Evanston, IL, 60208 (renee@earth.northwestern.edu); [2]NASA Marshall Space Flight Center, Huntsville, AL, 35812; [3]Qualis Corporation, Jacobs ESSSA Group, Huntsville, AL, 35806.

1.Introduction

KArLE (Potassium-Argon Laser Experiment) has been developed for in situ planetary geochronology using the K-Ar (potassium-argon) isotope system [1,2], where material ablated by LIBS (Laser-Induced Breakdown Spectroscopy) is used to calculate isotope abundances. We are determining the accuracy and precision of volume measurements of these pits using stereo and laser microscope data to better understand the ablation process for isotope abundance calculations. If a characteristic volume can be determined with sufficient accuracy and precision for specific rock types, KArLE will prove to be a useful instrument for future planetary rover missions.

2. Methodology

- 11 samples with 5 possible Martian analog compositions (basalt, jarosite, rhyolite, microcline, and tuff) were prepared by cutting an analysis surface and polishing to 1 mm.
- These compositions provide a range of hardness, heterogeneity, porosity, and grain size.
- We created a series of pits in each sample by firing a 1064nm Nd:YAG (neodymium-doped yttrium aluminum garnet) laser for 50 to 1350 shots per pit.
- Pit geometry and volumes were determined using a Keyence VK-X100 laser scanning microscope, utilizing both laser scanning and optical imaging techniques.
- Platinum tubes manufactured by Johnson Matthey Medical were used to test volume measurement error of the Keyence and operator, resulting in an average error of 5%.
- We conducted optical image analysis of several pits using the optical mode of the Keyence microscope and the Olympus SZX16 stereomicroscope to understand how pit volume could be reconstructed using the z-stacking method.

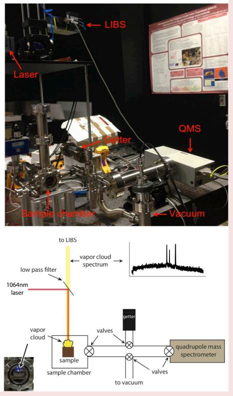

Figure 1: KArLE laboratory setup (above) and schematic (below; not to scale). See text for explanation.

3. Approach

Why K-Ar?

- The K-Ar isotope system is ideal for in situ age dating because:
  - The method is *not as technically difficult* as those for other isotope systems (e.g., Ar-Ar, U-Pb, Rb-Sr);
  - Ar is a noble gas and *easily extracted* from minerals;
  - It has a half life of 1.25 billion years, allowing a *wide range of geologic dating*.

KArLE Setup (Figure 1)

- LIBS uses high energy laser pulses to ablate a sample, creating a pit and producing a vapor cloud with excited atoms and ions that emit light at wavelengths specific to certain elements. This spectrum is used to estimate the elemental composition of the ablated sample.
  - We use LIBS to calculate the *relative* K abundance in wt% (weight percent).
  - The QMS (Quadrupole Mass Spectrometer) measures *absolute* Ar abundance, in mols, and is dependent on the mass that is ablated.
- To relate the QMS Ar measurement (mols) to the LIBS K measurement (wt%) we need to calculate the *total mass* of the ablated sample.
  - Some material may not ablate, so *calculating accurate mass may be difficult*.
  - Instead, we can *determine volume and density* to back calculate mass.
    - Bulk mineralogy or elemental composition can be used to calculate *density*.
    - This study is aimed towards developing a method to accurately and precisely determine *volume*.

4. Results

A. Pit Volume

- Jarosite and rhyolite are heterogeneous and/or porous samples and display nonlinear volume increase. Linear volume increases are observed for basalt and microcline.
- Although some samples are heterogeneous (like some basalt), they still behave fairly linearly because their heterogeneity is on a similar scale as the laser pit.
- Slopes of best fit lines for basalt and microcline (Fig. 2) are less than half those for jarosite and rhyolite and exhibit greater R^2 values, possibly suggesting similarities between materials.

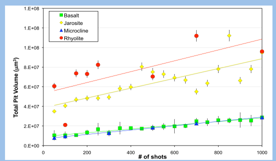

Figure 2: Average pit volume as a function of number of LIBS shots per pit for each sample.

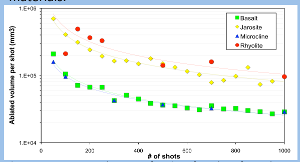

Figure 3: Average pit volume as a function of number of LIBS shots per pit for each sample.

- Although softer material forms deeper pits for the same number of LIBS shots than harder material (Fig. 3), there is an exponential trend for all materials that can be fairly well predicted if the relative hardness is known or estimated (e.g., the Specific Grind Energy based on the energy expended per volume removed using the MER Rock Abrasion Tool).

B. Pit Reconstruction

Functional fit

- A best-fit function is a Gaussian when considering only pit depth and width, but underestimates pit volume and introduces a volume uncertainty of about 30%.

Z-stacking

- With the Keyence microscope, a total of seven layers over a depth of 1209 mm were stacked to reconstruct a pit (Fig. 4a) with a calculated volume of 8.93E+07 mm³.
- With the Olympus stereomicroscope, we recovered thirteen layers over a depth of 1080 mm (Fig. 4b) and a calculated volume of 6.24E+07 mm³.
- Both calculated volumes agree within 20% of the reference volume (7.51E+07 mm³).

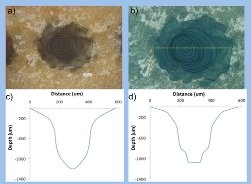

Figure 4: Reconstruction of Jarosite 500 shots pit using the Keyence VK-X100 optical microscope (a and c) and Olympus SZX16 stereomicroscope (b and d). X-Y resolution for (a) is 1.39 um/pixel and (b) 0.19 um/pixel.

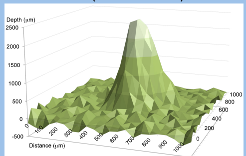

Figure 5: Basalt Sample 3 250 shots pit (inverted) downsampled to MAHLI stereo capability.

Stereo pair reconstruction

- Data was downsampled from the Keyence scanning microscope to the post spacing of a stereo model and MAHLI camera characteristics (Fig. 5).
- For each pixel, we calculated the volume to the reference surface as a simple prism under each pixel.
- This method is generally within 10% of the Keyence laser microscope-determined volume from z-stacking.

C. Compositional Effects

- Pits were generated with 200 LIBS shots on samples of jarosite (porphyritic), basalt sill (macrocrystalline, crystals ~few mm), and a core of Fish Canyon Tuff (macrocrystalline, crystals less than ~2 mm).
- Larger volumes ablated per shot are observed for Jarosite and decrease for Fish Canyon Tuff Core, with Basalt Sill 2 having the smallest.
- Larger variations in volume ablation occur for Jarosite 1 and Fish Canyon Tuff Core while Basalt Sill 2 exhibits a smaller range.

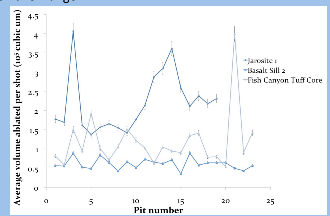

Figure 6: Average volume ablated per LIBS shot as a function of pit number. Each pit was generated with 200 LIBS shots; error bars are 5%.

5. Discussion

A. Variations in Pit Morphology

- Assuming a symmetric pit may be adequate for homogeneous samples with a large number of LIBS shots per pit (1000 LIBS shots on Microcline 2, Fig. 7) but can generate error for heterogeneous samples with less LIBS shots per pit.
- Figure 8 is data for the Basalt Sill 2 pit generated with 350 LIBS shots. The top image shows the pit was created along a grain boundary between plagioclase and pyroxene/amphibole. The lower images are topographic views (left is plan, right is a cross section) of the same pit showing the asymmetry in diameter with depth as a result of a change in mineralogy. This asymmetry is particularly apparent when compared with Fig. 7.

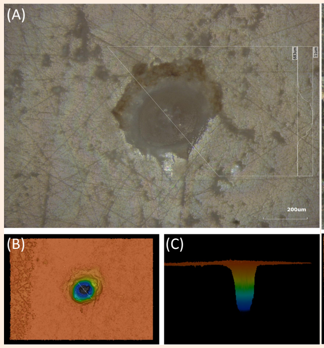

Figure 7: Microcline 2 pit created with 1000 laser shots. The pit is roughly symmetric and much deeper than in Figure 4, indicating important effects of composition and shot number on pit volume. (A) Optical view of pit with cross sectional profile; (B) 3D plan view of the pit, the line indicates the location of the profile in (A); (C) Cross sectional 3D view of the profile in (A).

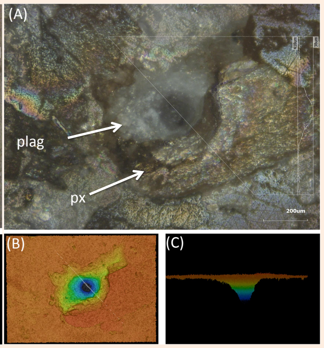

Figure 8: Basalt Sill 2 pit created with 350 laser shots. Note the difference in pit morphology where the composition changes from plag (plagioclase) to px (pyroxene), affecting overall pit volume (Figure 2). (A) Optical view of pit with cross sectional profile; (B) 3D plan view of the pit, the line indicates the location of the profile in (A); (C) Cross sectional 3D view of the profile in (A).

6. Summary

Critical to the success of the KArLE experiment, or any LIBS-MS geochronology investigation [e.g., 3-4], is the accurate measurement of the LIBS-ablated pit. This study shows that either z-stacking or stereo imaging using available micro-imaging cameras are suitable methods for determining the volume of LIBS pits in flight designs (Fig. 9). In a pinch, material properties (hardness, heterogeneity, porosity, and grain size) can be used to estimate the likely range of pit volume per shot and a functional fit using pit width and depth can estimate the pit volume within a larger uncertainty.

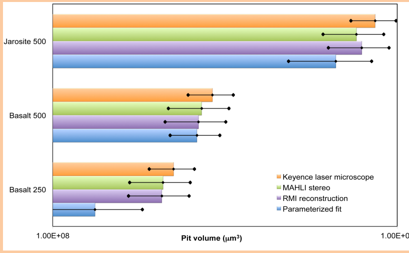

Figure 9: Comparison of volume calculation methods.

7. Acknowledgements

The majority of this work was completed during the summer of 2013 as part of the Marshall Space Flight Center Summer Internship program in Huntsville, Alabama. Discussions with Zheng-Hua Li helped refine methods that contributed to the foundation of this project.

8. References

[1] Cohen B. A. et al. (2013) *LPSC XLIV,* Abstract #2363. [2] Cohen B. A. et al. (2012) Int'l Workshop on Instru. for Planetary Missions, Abstract #1018. [3] Cho Y. et al. (2012) Int'l Workshop on Instru. for Planetary Missions, Abstract #1093. [4] Devismes D. et al. (2013) European Planetary Science Congress 8, Abstract EPSC2013-2071.